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(54) Title: PRODUCTION OF DETERGENT GRANULATES (57) Abstract <p>A process of forming granular detergent products, the process comprising, in a gas fluidisation granulator, contacting a fluidised particulate solid material with a spray of liquid binder, whilst fluidising the solids in the granulator with at least one gas stream, wherein the gas temperature is controlled so as to be increased and/or reduced during at least one stage of the process.</p>		

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PRODUCTION OF DETERGENT GRANULATES

The present invention relates to a process for the production of granular detergent compositions.

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It is long known in the art to obtain detergent powders by spray drying. However, the spray-drying process is both capital and energy intensive and consequently the resultant product is expensive.

10

More recently, there has been much interest in production of granular detergent products by processes which employ mainly mixing, without the use of spray drying. These mixing techniques can offer great flexibility in producing powders of various different compositions from a single plant by post-dosing various components after an initial granulation stage.

A known kind of mixing process, which does not involve spray drying, employs a moderate-speed granulator (a common example often colloquially being called a "ploughshare"), optionally preceded by a high-speed mixer (a common example often colloquially being called a "recycler" due to its recycling cooling system). Typical examples of such processes are described in our European patent specifications EP-A-367 339, EP-A-390 251 and EP-A-420 317. These moderate-speed and high-speed mixers exert relatively high levels of shear on the materials being processed.

Until recently, there has been less effort in developing use of low-shear mixers or granulators. One kind of process, which does not involve spray-drying, involves use of a low-shear granulator of the gas fluidisation kind. In this kind of apparatus, a gas (usually air) is blown through a body of particulate solids onto which is sprayed a liquid component.

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A gas fluidisation granulator is sometimes called a "fluidised bed" granulator or mixer. However, this is not strictly accurate since such mixers can be operated with a gas flow rate so high that a classical "bubbling" fluid bed
5 does not form.

Although gas fluidisation granulators can give good control of bulk density, there is still a need for greater flexibility and in particular, for producing lower bulk
10 density powders. Processes involving low-shear granulation are quite varied.

For example, WO96/04359 (Unilever) discloses a process whereby low bulk density powders are prepared by contacting a
15 neutralising agent such as an alkaline detergency builder and a liquid acid precursor of an anionic surfactant in a fluidisation zone to form detergent granules.

Nevertheless, as pointed-out in Indian Patent No. 166307
20 (Unilever), use of a conventional gas fluidisation process can lead to formation of lumps and sticky granules. The latter document seeks to overcome this problem by using an internal recirculation gas fluidisation granulator. However, the present invention overcomes this problem more simply and
25 effectively by controlling the gas temperature.

Thus, the present invention now provides a process of forming a granular detergent products, the process comprising, in a gas fluidisation granulator, contacting a fluidised
30 particulate solid material with a spray of liquid binder, whilst fluidising the solids in the granulator with at least one gas stream, wherein the gas temperature is controlled so as to be increased and/or reduced during at least one stage of the process.

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- Preferably, controlling the gas temperature according to the present invention leads to an increase and/or reduction in the temperature of the fluidising particulate solid material during at least one stage of the process. In other words,
- 5 the gas temperature is controlled not so as to merely maintain a constant "bed" temperature, for example by removing heat of reaction, but so as to increase and/or decrease the actual temperature of the fluidising solids.
- 10 The gas fluidisation granulation apparatus basically comprises a chamber in which a stream of gas, usually air, is used to cause turbulent flow of particulate solids to form a "cloud" of the solids and liquid binder is sprayed onto or into the cloud to contact the individual particles. As the
- 15 process progresses, individual particles of solid starting materials become agglomerated, due to the liquid binder, to form granules.
- The process of the present invention resolves the stickiness of the granules as they form. In many cases, it is believed that this may occur as a result of transformation of the liquid constituents into a more solid state or a state having a higher viscosity, due to the temperature variation of the process.
- 20
- 25 The temperature increase and/or reduction must occur during at least one stage of the process, i.e. at least one stage when fluidisation and spraying are in progress.
- 30 The process may be operated with a gas temperature below ambient during at least one stage (or all of) the process. Preferably, it is operated with a gas temperature higher during a first stage of the process than during a second stage, before or after the first stage.

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The gas fluidisation granulator is typically operated at a superficial air velocity of about $0.1-1.2 \text{ ms}^{-1}$, either under positive or negative relative pressure. The gas temperature, and thus preferably the bed temperature, may be elevated for a first period, e.g. at up to 80°C or even up to 200°C and then at one or more other stages (before or after), it may be reduced to just above, at, or below ambient, e.g. to 30°C or less, preferably 25°C or less or even as low as 5°C or less or -10°C or less.

10

In a preferred embodiment, the gas temperature, and preferably also the bed temperature, is elevated for a first period and subsequently lowered in a second period.

15 When the process is a batch process, the temperature variation will be effected over time. If it is a continuous process, it will be varied along the "track" of the granulator bed. In the latter case, this is conveniently effected using a granulator of the "plug flow" type, i.e. one
20 in which the materials flow through the reactor from beginning to end.

In a batch process, the gas temperature may be reduced over a relatively short period of time, for example 10 to 50% of the
25 process time. Typically, the gas temperature may be reduced for 0.5 to 15 minutes. In a continuous process, the gas temperature may be reduced along a relatively short length of the "track" of the granulator bed, for example along 10 to 50% of the track. In both cases, the gas may be pre-cooled.

30

Preferably, the gas temperature, and preferably also the bed temperature, is not lowered until granulation of the fluidising particulate solid material is substantially complete.

- 5 -

As used herein, the term "bed temperature" refers to the temperature of the fluidising solid particulate material. The temperature of the fluidising solid particulate material can be measured, for example, using a thermocouple probe.

5 Whether there is a discernible powder bed or no discernible powder bed (i.e. because the mixer is being operated with a gas flow rate so high that a classical "bubbling" fluid bed is not formed), the "bed temperature" is taken to be the temperature as measured at a point inside the fluidisation

10 chamber about 15 cm from the gas distributor plate.

In the context of the present invention, the term "granular detergent product" encompasses granular finished products for sale, as well as granular components or adjuncts for forming

15 finished products, e.g. by post-dosing to or with, or any other form of admixture with further components or adjuncts. Thus a granular detergent product as herein defined may, or may not contain detergent material such as synthetic surfactant and/or soap. The minimum requirement is that it

20 should contain at least one material of a general kind of conventional component of granular detergent products, such as a surfactant (including soap), a builder, a bleach or bleach-system component, an enzyme, an enzyme stabiliser or a component of an enzyme stabilising system, a soil anti-

25 redeposition agent, a fluorescer or optical brightener, an anti-corrosion agent, an anti-foam material, a perfume or a colourant.

As used herein, the term "powder" refers to materials

30 substantially consisting of grains of individual materials and mixtures of such grains. The term "granule" refers to a small particle of agglomerated powder materials. The final product of the process according to the present invention consists of, or comprises a high percentage of granules.

35 However, additional granular and or powder materials may

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optionally be post-dosed to such a product. Moreover, as will be explained in more detail hereinbelow, solid starting materials of the present invention are particulate and may be powdered and/or granular.

5

Whether the gas fluidisation granulation process of the present invention is a batch process or a continuous process, particulate solid starting material may be introduced at any time during the time when liquid binder is being sprayed. In
10 the simplest form of process, solid starting material is first introduced to the gas fluidisation granulator and then sprayed with the liquid binder. However, some particulate solid starting material could be introduced at the beginning of processing in the gas fluidisation apparatus and the
15 remainder introduced at one or more later times, either as one or more discrete batches or in continuous fashion.

Suitably, the solid starting material(s) have a particle size distribution such that not more than 5% by weight of the
20 particles have a particle size greater than 250 μm . It is also preferred that at least 30% by weight of the particles have a particle size below 100 μm , more preferably below 75 μm . However the present invention is also usable with larger fractions of solid starting materials (i.e. > 5% more than
25 250 μm , optionally also < 30% below 100 μm or 75 μm) but this increases the chance of some crystals of unagglomerated starting materials being found in the final product. This presents a cost benefit in allowing use of cheaper raw materials. In any event, the particulate solid starting
30 material(s) have an average particle size below 500 μm to provide detergent powders having a particularly desired low bulk density. Within the context of solid starting materials, reference to an average particle size means the $d_{3,2}$ average particle diameter.

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The gas fluidisation granulator may be adapted to recycle "fines" i.e. powdered or part-granular material of very small particle size, so that they are returned to the input of the gas fluidisation apparatus and/or input of any pre-mixer.

- 5 Preferably the fine particulates are elutriated material, i.e. they are present in the air leaving a the gas fluidisation chamber.

- 10 The gas fluidisation granulator may optionally be of the kind provided with a vibrating bed, particularly for use in continuous mode.

- 15 In a preferred class of processes according to the present invention, the liquid binder comprises an acid precursor of an anionic surfactant and the particulate solid starting material comprises an inorganic alkaline material. The process of the present invention is especially suited to this kind of granulation, especially when the temperature is elevated in the first part of the process. In that way, the
20 neutralisation reaction can proceed much nearer to completion, before the end of the granulation operation, than would otherwise be the case.

- 25 It is thus preferred that bed temperature is increased by increasing the gas temperature during any neutralisation reaction, preferably for a substantial part of the neutralisation reaction.

- 30 The acid precursor may for example be the acid precursor of a linear alkylbenzene sulphonate (LAS) or primary alkyl sulphate (PAS) anionic surfactant or of any other kind of anionic surfactant.
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Suitable materials for use as the inorganic alkaline material include alkali metal carbonates and bicarbonates, for example sodium salts thereof.

- 5 The neutralising agent is very preferably present at a level sufficient to neutralise fully the acidic component. If desired, a stoichiometric excess of neutralising agent may be employed to ensure complete neutralisation or to provide an alternative function, for example as a detergency builder,
10 e.g. if the neutralising agent comprises sodium carbonate.

- The liquid binder may alternatively or additionally contain one or more other liquid materials such as liquid nonionic surfactants and/or organic solvents. The total amount of
15 acid precursor will normally be as high as possible, subject to the presence of any other components in the liquid and subject to other considerations referred to below. Thus, the acid precursor may constitute at least 98% (e.g. at least 95%) by weight of the liquid binder, but could be at least
20 75%, at least 50% or at least 25% by weight of the binder. It can even, for example, constitute 5% or less by weight of the binder. Of course the acid precursor can be omitted altogether if required.

- 25 When liquid nonionic surfactant is present in the liquid binder together with an acid precursor of an anionic surfactant, then the weight ratio of all acid precursor(s) to nonionic surfactants, will normally be from 20:1 to 1:20. However, this ratio may be, for example, 15:1 or less (of the
30 anionic), 10:1 or less, or 5:1 or less. On the other hand, the nonionic may be the major component so that the ratio is 1:5 or more (of the nonionic), 1:10 or more, or 1:15 or more. Ratios in the range from 5:1 to 1:5 are also possible.

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For manufacture of granules containing anionic surfactant, sometimes it will be desirable not to incorporate all of such anionic by neutralisation of an acid precursor. Some can optionally be incorporated in the alkali metal salt form, dissolved in the liquid binder or else as part of the solids. In that case, the maximum amount of anionic incorporated in the salt form (expressed as the weight percentage of total anionic surfactant salt in the product output from the gas fluidisation granulator) is preferably no more than 70%, more preferably no more than 50% and most preferably no more than 40%.

If it is desired to incorporate a soap in the granules, this can be achieved by incorporating a fatty acid, either in solution in the liquid binder or as part of the solids. The solids in any event must then also comprise an inorganic alkaline neutralising agent to react with the fatty acid to produce the soap.

The liquid binder will often be totally or substantially non-aqueous, that is to say, any water present does not exceed 25% by weight of the liquid binder, but preferably no more than 10% by weight. However, if desired, a controlled amount of water may be added to facilitate neutralisation.

Typically, the water may be added in amounts of 0.5 to 2% by weight of the final detergent product. Any such water is suitably added prior to or together or alternating with the addition of the acid precursor.

Alternatively, an aqueous liquid binder may be employed. This is especially suited to manufacture of products which are adjuncts for subsequent admixture with other components to form a fully formulated detergent product. Such adjuncts will usually, apart from components resulting from the liquid binder, mainly consist of one, or a small number of

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components normally found in detergent compositions, e.g. a surfactant or a builder such as zeolite or sodium tripolyphosphate. However, this does not preclude use of aqueous liquid binders for granulation if substantially fully formulated products. In any event, typical aqueous liquid binders include aqueous solutions of alkali metal silicates, water soluble acrylic/maleic polymers (e.g. Sokalan CP5) and the like.

10 In a refinement of the process of the present invention, the particulate solid starting material may be contacted and mixed with a first portion of the liquid binder, e.g. in a low-, moderate- or high-shear mixer (i.e. a pre-mixer) to form a partially granulated material. The latter can then be
15 sprayed with a second portion of the liquid binder in the gas fluidisation granulator, to form the granulated detergent product.

In such a two-stage granulation process, it is preferred, but
20 not absolutely necessary, for the total of liquid binder to be dosed only in the partial granulation pre-mixer and fluidisation steps. Conceivably, some could be dosed during or before partial granulation premixing and/or fluidisation. Also, the content of the liquid binder could be varied
25 between these first and second stages.

The extent of granulation in the pre-mixer (i.e. partial granulation) and the amount of granulation in the gas fluidisation granulator is preferably determined in
30 accordance with the final product density desired. Preferred amounts of liquid binder to dosed at each of the two stages may be varied thus:-

(i) If a lower powder density is desired, i.e. 350-650 g/l

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- 5 (a) 5-75% by weight of total liquid binder is preferably added in the pre-mixer; and
(b) the remaining 95-25% by weight of total liquid binder is preferably added in the gas fluidisation granulator.

- (ii) If a higher powder density is desired, i.e. 550-1300 g/l
10 (a) 75-95% by weight of total liquid binder is preferably added in the pre-mixer; and
(b) the remaining 25-5% by weight of total liquid binder is preferably added in the gas fluidisation granulator.

If an initial pre-mixer is used for partial granulation, an
15 appropriate mixer for this step is a high-shear Lodige^R CB machine or a moderate-speed mixer such as a Lodige^R KM machine. Other suitable equipment include Drais^R T160 series manufactured by Drais Werke GmbH, Germany; the Littleford mixer with internal chopping blades and turbine-type miller
20 mixer having several blades on an axis of rotation. A low- or high-shear mixer granulator has a stirring action and/or a cutting action which are operated independently of one another. Preferred types of low- or high-shear mixer/ granulators are mixers of the Fukae^R FS-G series; Diosna^R V
25 series ex Dierks & Sohne, Germany; Pharma Matrix^R ex T.K. Fielder Ltd; England. Other mixers believed to be suitable for use in the process of the invention are Fuji^R VG-C series ex Fuji Sangyo Co., Japan; the Roto^R ex Zanchetta & Co. srl, Italy and Schugi^R Flexomix granulator.

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Yet another mixer suitable for use in a pre-granulation stage is the Lodige (Trade Mark) FM series (ploughshare mixers) batch mixer ex Morton Machine Co. Ltd., Scotland.

- 5 Optionally, a "layering agent" or "flow aid" may be introduced at any appropriate stage. This is to improve the granularity of the product, e.g. by preventing aggregation and/or caking of the granules. Any layering agent flow aid is suitably present in an amount of 0.1 to 15% by weight of
10 the granular product and more preferably in an amount of 0.5 to 5%.

Suitable layering agents/flow aids include crystalline or amorphous alkali metal silicates, aluminosilicates including
15 zeolites, Dicalol, calcite, diatomaceous earths, silica, for example precipitated silica, chlorides such as sodium chloride, sulphates such as magnesium sulphate, carbonates such as calcium carbonate and phosphates such as sodium tripolyphosphate. Mixtures of these materials may be employed
20 as desired.

In general, additional components may be included in the liquid binder or admixed with the solid neutralising agent at an appropriate stage of the process. However, solid
25 components can be post-dosed to the granular detergent product.

In addition to any anionic surfactant which optionally may be produced by a neutralisation step, further anionic
30 surfactants, or nonionic surfactant as mentioned above, also, cationic, zwitterionic, amphoteric or semipolar surfactants and mixtures thereof may be added at a suitable time. In general suitable surfactants include those generally described in "Surface active agents and detergents" Vol I by
35 Schwartz and Perry. As mentioned above if desired, soap

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derived from saturated or unsaturated fatty acids having, for example having an average of C_{10} to C_{18} carbon atoms may also be present.

- 5 If present, the detergent active is suitably incorporated at a level of 5 to 40%, preferably 10 to 30% by weight of the final granular detergent product.

10 A complete detergent composition often contains a detergency builder. Such a builder may be introduced with the solid material and/or added subsequently as desired. The builder may also constitute a neutralising agent, for example sodium carbonate, in which case sufficient material will be employed for both functions.

15 Generally speaking, the total amount of detergency builder in the granular product is suitably from 5 to 95%, for example from 10 to 80%, preferably from 15 to 65%, more preferably from 15 to 50% by weight.

20 Inorganic builders that may be present include sodium carbonate, if desired in combination with a crystallisation seed for calcium carbonate as disclosed in GB-A-1 437 950. Any sodium carbonate will need to be in excess of any used to
25 neutralise the anionic acid precursor if the latter is added during the process.

Other suitable builders include crystalline and amorphous aluminosilicates, for example zeolites as disclosed in
30 GB-A-1 473 201; amorphous aluminosilicates as disclosed in GB-A-1 473 202; and mixed crystalline/amorphous aluminosilicates as disclosed in GB 1 470 250; and layered silicates as disclosed in EP-B-164 514. Inorganic phosphate builders, for example, sodium, orthophosphate, pyrophosphate

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and tripolyphosphate, may also be present, but on environmental grounds those are no longer preferred.

Aluminosilicates, whether used as layering agents and/or
5 incorporated in the bulk of the particles may suitably be present in a total amount of from 10 to 60% and preferably an amount of from 15 to 50% by weight. The zeolite used in most commercial particulate detergent compositions is zeolite A. Advantageously, however, maximum aluminium zeolite P (zeolite
10 MAP) described and claimed in EP-A-384 070 may be used. Zeolite MAP is an alkali metal aluminosilicate of the P type having a silicon to aluminium ratio not exceeding 1.33, preferably not exceeding 1.15, and more preferably not exceeding 1.07.

15 Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di-
20 and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts. A copolymer of maleic acid, acrylic acid and vinyl acetate is especially
25 preferred as it is biodegradable and thus environmentally desirable. This list is not intended to be exhaustive.

Especially preferred organic builders are citrates, suitably used in amounts of from 5 to 30%, preferably from 10 to 25%
30 by weight; and acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15%, preferably from 1 to 10% by weight. Citrates can also be used at lower levels (eg 0.1 to 5%) by weight for other purposes. The builder is preferably present in alkali
35 metal salt, especially sodium salt, form.

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Suitably, the builder system may also comprise a crystalline layered silicate, for example, SKS-6 ex Hoechst, a zeolite, for example, zeolite A and optionally an alkali metal citrate.

5

The granular composition resulting from the process of the present invention may also comprise a particulate filler (or any other component which does not contribute to the wash process) which suitably comprises an inorganic salt, for
10 example sodium sulphate and sodium chloride. The filler may be present at a level of 5 to 70% by weight of the granular product.

The present invention also encompasses a granular detergent
15 product resulting from the process of the invention (before any post-dosing or the like). This product will have a bulk density determined by the exact nature of the process. If the process does not involve a pre-mixer to effect partial granulation, a final bulk density of 350-750 g/l can normally
20 be expected. As mentioned above, use of a pre-mixer enables the final bulk density to be 350-650 g/l or 550-1300 g/l, respectively, according to whether option (i) or (ii) is utilised. However, granular detergent products resulting from the present invention are also characterised by their
25 particle size ranges. Preferably not more than 10% by weight has a diameter > 1.4 mm and more preferably, not more than 5% by weight of the granules are above this limit. It is also preferred that not more than 20% by weight of the granules have a diameter > 1 mm. Finally, the granules can be
30 distinguished from granules produced by other methods by mercury porosimetry. The latter technique cannot reliably determine the porosity of individual unagglomerated particles but is ideal for characterising the granules.

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A fully formulated detergent composition produced according to the invention might for example comprise the detergent active and builder and optionally one or more of a flow aid, a filler and other minor ingredients such as colour, perfume, fluorescer, bleaches, enzymes.

The invention will now be illustrated by the following non-limiting examples:

10 Examples

The following formulation was produced:

	Sodium-LAS	24 wt%
15	Sodium-Carbonate	32 wt%
	STPP	32 wt%
	Zeolite 4A	10 wt%
	water	2 wt%

20 In examples I to IV, the fluidising air temperature was varied from 20°C to 80°C in the first stage followed by a second stage at 20°C. A Spraying System nozzle SUE25 was used operating with an atomising air pressure of 5 bar.

25 The following influence on the powder was observed in batch experiments:

Example		I	II	III	IV
LAS addition rate	[gmin ⁻¹]	1280	1600	1320	1600
First stage	[s]	139	112	135	112
First stage temperature	[°C]	20	20	80	80
Second stage	[s]	60	60	60	60
Second stage temperature	[°C]	20	20	20	20
UCT*	[g]	7200	7100	4350	4700

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*UCT is a measure of stickiness, the higher the value, the more sticky the product. Example I and II are control examples where there was no temperature variation.

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CLAIMS

1. A process of forming a granular detergent products, the process comprising, in a gas fluidisation granulator,
5 contacting a fluidised particulate solid material with a spray of liquid binder, whilst fluidising the solids in the granulator with at least one gas stream, wherein the gas temperature is controlled so as to be increased and/or reduced during at least one stage of the process.
10
2. A process according to claim 1, wherein the gas temperature is controlled so as increase and/or reduce the temperature of the fluidising particulate solid material during at least one stage of the process.
15
3. A process according to claim 2, wherein the temperature of the fluidising particulate solid material is reduced to below or at ambient during the at least one stage.
- 20 4. A process according to claim 2, wherein the temperature of the fluidising particulate solid material is higher during a first stage of the process than during a second stage of the process, after the first stage.
- 25 5. A process according to claim 4, wherein the process is a batch process and the temperature change between the first and second stages is made over time.
- 30 6. A process according to claim 4, wherein the process is a continuous process and the temperature change between the first and second stages is made along the granulation track.
- 35 7. A process according to claim 5, when effected in a plug flow granulator.

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8. A process according to any one of claims 4 to 7, wherein the temperature in the first stage is controlled so as to be up to 200°C, preferably up to 80°C.
- 5 9. A process according to any one of claims 4 to 8, wherein the temperature in the second stage is controlled so as to be 30°C or less, preferably 25°C or less, or 5°C or less or -10°C or less.
- 10 10. A process according to claim 1, wherein the gas temperature is reduced to below or at ambient during the at least one stage.
- 15 11. A process according to claim 1, wherein the gas temperature is higher during a first stage of the process than during a second stage of the process, before or after the first stage.
- 20 12. A process according to claim 11, wherein the process is a batch process and the temperature change between the first and second stages is made over time.
- 25 13. A process according to claim 11, wherein the process is a continuous process and the temperature change between the first and second stages is made along the granulation track.
- 30 14. A process according to claim 13, when effected in a plug flow granulator.
15. A process according to any one of claims 11 to 14, wherein the temperature in the first stage is controlled so as to be up to 200°C, preferably up to 80°C.

- 20 -

16. A process according to any one of claims 10 to 15,
wherein the temperature in the second stage is
controlled so as to be 30°C or less, preferably 25°C or
less, or 5°C or less or -10°C or less.
- 5
17. A process according to any preceding claim, wherein the
liquid binder comprises an acid precursor of an anionic
surfactant and the particulate solids comprise an
inorganic alkaline material.
- 10
18. A process according to any preceding claim, wherein a
first portion of the liquid binder is admixed with a
particulate solid starting material in a pre-mixer to
form a partially granular solid material and then a
15 second portion of the liquid binder is sprayed to
contact the partially granular solid material in the gas
fluidisation granulator to effect complete granulation.
19. A granular detergent product produced by a process
20 according to any preceding claim.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 98/03669

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D11/00 C11D17/06 C11D11/04

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 209 172 A (UNILEVER PLC) 4 May 1989 see claims; examples ---	1,5,6, 17,19
A	EP 0 345 090 A (COLGATE PALMOLIVE CO) 6 December 1989 see claims 1-7,16,17 ---	1,6,17, 19
A	WO 96 04359 A (UNILEVER) 15 February 1996 cited in the application see claims ---	1,6,17, 19
A	GB 1 341 557 A (THE DANISH OIL MILLS AND SOAP FACTORIES LTD.) 25 December 1973 see claims 1-13 -----	1,6,17, 19

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

26 October 1998

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 98/03669

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 2209172	A	04-05-1989	NONE	
EP 0345090	A	06-12-1989	US 4919847 A	24-04-1990
			AU 623904 B	28-05-1992
			AU 3470789 A	07-12-1989
			CA 1324745 A	30-11-1993
			DK 273289 A	04-12-1989
			JP 2029500 A	31-01-1990
			MX 166128 B	21-12-1992
			NO 174213 B	20-12-1993
WO 9604359	A	15-02-1996	AU 3165695 A	04-03-1996
			BR 9508505 A	26-05-1998
			CA 2195313 A	15-02-1996
			CZ 9700305 A	17-09-1997
			EP 0775193 A	28-05-1997
			HU 77715 A	28-07-1998
			PL 318548 A	23-06-1997
			SK 14597 A	09-07-1997
GB 1341557	A	25-12-1973	NONE	